



Aalborg Universitet

AALBORG UNIVERSITY  
DENMARK

## Water Defluoridation

### *Nanofiltration vs Membrane Distillation*

Ayala, Lucía I. Moran ; Paquet, Marie; Janowska, Katarzyna Joanna; Paul, Jamard; Quist-Jensen, Cejna Anna; Bosio, Gabriela N. ; Martire, Daniel O. ; Fabbri, Debora; Boffa, Vittorio

*Published in:*  
Industrial & Engineering Chemistry Research

*DOI (link to publication from Publisher):*  
[10.1021/acs.iecr.8b03620](https://doi.org/10.1021/acs.iecr.8b03620)

*Publication date:*  
2018

*Document Version*  
Publisher's PDF, also known as Version of record

[Link to publication from Aalborg University](#)

### *Citation for published version (APA):*

Ayala, L. I. M., Paquet, M., Janowska, K. J., Paul, J., Quist-Jensen, C. A., Bosio, G. N., Martire, D. O., Fabbri, D., & Boffa, V. (2018). Water Defluoridation: Nanofiltration vs Membrane Distillation. *Industrial & Engineering Chemistry Research*, 57(43), 14740-14748. <https://doi.org/10.1021/acs.iecr.8b03620>

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal -

### **Take down policy**

If you believe that this document breaches copyright please contact us at [vbn@aub.aau.dk](mailto:vbn@aub.aau.dk) providing details, and we will remove access to the work immediately and investigate your claim.

# Water Defluoridation: Nanofiltration vs Membrane Distillation

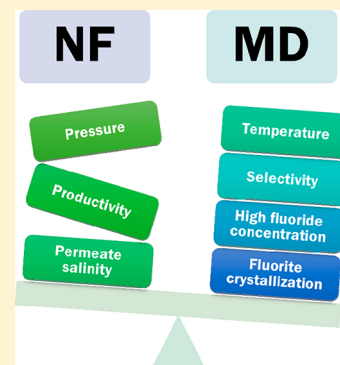
Lucía I. Moran Ayala,<sup>†</sup> Marie Paquet,<sup>‡</sup> Katarzyna Janowska,<sup>‡</sup> Paul Jamard,<sup>‡</sup> Cejna A. Quist-Jensen,<sup>‡</sup> Gabriela N. Bosio,<sup>†</sup> Daniel O. Mártire,<sup>†</sup> Debora Fabbri,<sup>§</sup> and Vittorio Boffa<sup>\*,‡,§</sup>

<sup>†</sup>Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas (INIFTA), CONICET, Universidad Nacional de La Plata, Diagonal 113 y calle 64, 1900, La Plata, Argentina

<sup>‡</sup>Department of Chemistry and Bioscience, Aalborg University, Fredrik Bajers vej 7H, 9220 Aalborg, Denmark

<sup>§</sup>Dipartimento di Chimica, Università di Torino, Via P. Giuria 5, 10125 Torino, Italy

**ABSTRACT:** Nowadays, fluoride contamination of drinking water is a major problem for various countries, because high concentrations of fluoride pose a risk of dental and skeletal fluorosis. Over past years, membrane nanofiltration (NF) has been proposed as convenient defluoridation technology. However, NF cannot be applied to water systems with high fluoride concentration, and the disposal of the membrane concentrate remains an issue. In this work, we compared a commercial polyester NF membrane and a polypropylene hollow-fiber membrane distillation (MD) module for their ability to remove fluoride ions from water in the presence of hardness ions and organic fouling agents. The NF membrane can offer more than 10 times higher water productivity than MD, under realistic gradients of temperature and pressure, respectively. Despite that, after reaching a concentration factor of about 3, fouling and scaling caused the flux to drop to about 80% with respect to its initial value. Moreover,  $F^-$  retention decreased from 90% to below 80%, thus providing a permeate of scarce quality. MD was operated in the direct-contact mode on a polypropylene hollow-fiber membrane, which was charged with a hot feed flow (average  $T = 58\text{ }^{\circ}\text{C}$ ) on one side and a cooled ( $20\text{ }^{\circ}\text{C}$ ) permeate flow of distilled water on the other side. The concentration of fluoride ions in the permeate was always below the detection limit of our electrode (0.2 ppm), regardless of the fluoride concentration in the feed. Moreover, the MD module showed higher resistance to fouling and scaling than NF, and  $\text{CaF}_2$  crystals were recovered from the MD concentrate after cooling. These results suggest that the synergic combination of the two techniques might be beneficial for the purification of fluoride-contaminated water systems: MD can be used to further concentrate the NF retentate, thus producing high-purity water and recovering  $\text{CaF}_2$  crystals.



## INTRODUCTION

Contamination of drinking water by fluoride is associated with health hazards such as dental and skeletal fluorosis.<sup>1,2</sup> High fluoride concentration in natural water can be caused by geogenic sources (as leaching of fluorine-containing minerals in rocks and sediments) and anthropogenic sources, mainly due to the use of pesticides and to industrial activities. Thus, nowadays, fluoride contamination of drinking water is a major problem for various countries,<sup>3</sup> including Argentina, Mexico, the United States, Middle East countries, China, and India. The World Health Organization (WHO) indicates the limits of fluoride concentration in drinking water between 0.5 and 1.0  $\text{mg L}^{-1}$  and recommends setting local guidelines at a concentration lower than 1.5  $\text{mg L}^{-1}$ .<sup>4,5</sup> Hence, various technologies have been proposed for the abatement and the control of fluoride,<sup>6</sup> such as adsorption, ion exchange, chemical precipitation, and a range of membrane processes encompassing reverse osmosis (RO), nanofiltration (NF), electrodialysis, and really recently membrane distillation (MD). Efficiency and productivity of these processes is governed by different factors, such as raw water characteristics, pressure, temperature, etc.

One of the emerging processes is NF, which has been applied to water defluoridation with promising results on the

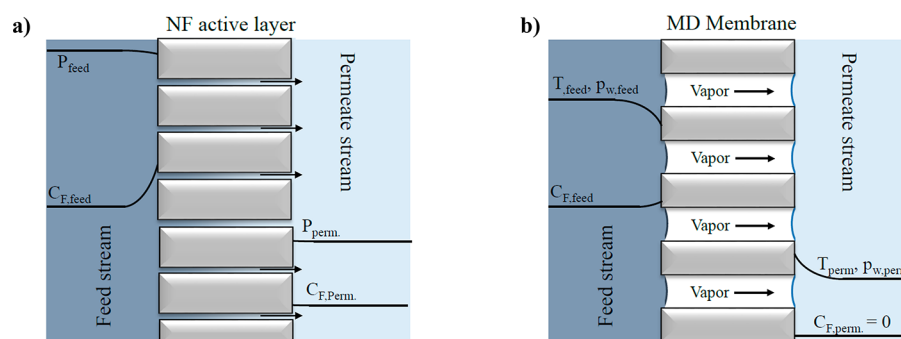
laboratory and pilot scale, over the past decade.<sup>7–20</sup> NF is a pressure-driven process, in which the contaminants are removed by a water-permeable membrane. NF membranes have typically 1–2 nm diameter pores, that is, larger than the size of hydrated ions (e.g., the effective size of hydrated fluoride<sup>21–23</sup> ions is  $\sim 0.3\text{ nm}$ ). Therefore, their selectivity depends on a combination of steric and charge interactions,<sup>24–26</sup> which allow removing hardness ions and reducing the concentration of monovalent ions (as fluoride). NF membranes have lower ion rejection than reverse osmosis (RO) membranes but can offer several advantages, such as low operating pressure, high permeability, and relatively low costs of investment, operation, and maintenance.<sup>26,27</sup> The two main drawbacks of NF membranes are the following: (i) the quality of the produced water is affected by the fluoride concentration in the feed; (ii) their productivity is reduced by concentration-polarization phenomena. In short, due to the water permeation, salt concentration increases in the vicinity of the

**Received:** August 2, 2018

**Revised:** October 5, 2018

**Accepted:** October 9, 2018

**Published:** October 10, 2018



**Figure 1.** Cross-sectional diagrams of fluoride concentration ( $C_F$ ), hydraulic pressure ( $P$ ), water vapor pressure ( $p_w$ ), and temperature ( $T$ ) of the feed and permeate side for (a) NF active layer and (b) MD membrane.

membrane surface, thus resulting in an increased salt concentration in the permeate, which corresponds to a decrease in the observed retention. Moreover, scaling and fouling require frequent backwashing and cleaning to the detriment of membrane service time and productivity.

In this context, membrane distillation (MD) has been recently proposed as a possible alternative to NF and RO in desalination<sup>28,29</sup> and defluoridation<sup>30–32</sup> processes. The cross-sectional diagrams of NF and MD are depicted in Figure 1, in order to stress the main differences between the two processes. MD is an emerging technology, which is based on the transport of water vapor through a hydrophobic macroporous membrane. In this case, membrane pores have a size that is 2 orders of magnitude larger than the hydrated ions, thus size exclusion and charge interaction do not contribute to the separation mechanism. Indeed, the distillation membrane acts as a barrier between the hot polluted solution and the cold permeate.<sup>33–35</sup> Due to its hydrophobic properties, the membrane is not permeable to water in the liquid state but allows for steam permeation. Mass and heat transfer mechanisms govern steam flux from the hot feed to the cold permeate side of the membrane. The main advantage of MD is the ability to operate at a lower operating feed temperature than conventional distillation and a much lower hydrostatic pressure than NF and RO.<sup>36</sup> Moreover, MD permeability and selectivity are both negligibly affected by the increase of osmotic pressure and concentration polarization phenomena during the feed concentration.<sup>37</sup> On the other hand, temperature polarization has a negative impact on the water productivity of MD systems.

The aim of this work is to assess the advantages and the limits of MD in filtering fluoride-contaminated water by a direct comparison with a benchmark NF module. Hence, two membranes, namely, a macroporous hollow fiber polypropylene MD and a microporous polyamide over polysulfone NF membrane,<sup>38</sup> were tested for their ability to remove fluoride ions in the presence of hardness ions and organic fouling agents.

## 2. EXPERIMENTAL SECTION

**2.1. Nanofiltration Tests.** Nanofiltration tests were performed with a cross-flow filtration setup, which was assembled in our laboratories, over polyester NF membranes (Alfa Laval,  $\geq 99\%$  rejection of  $\text{MgSO}_4$  at 2000 ppm, 9 bar, and  $25^\circ\text{C}$ ). Two disc membranes (total filtering area  $0.072\text{ m}^2$ ) were sealed in a plate and frame module (Alfa Laval - LabStak M20). Feed was pumped to the membrane by the feed pump

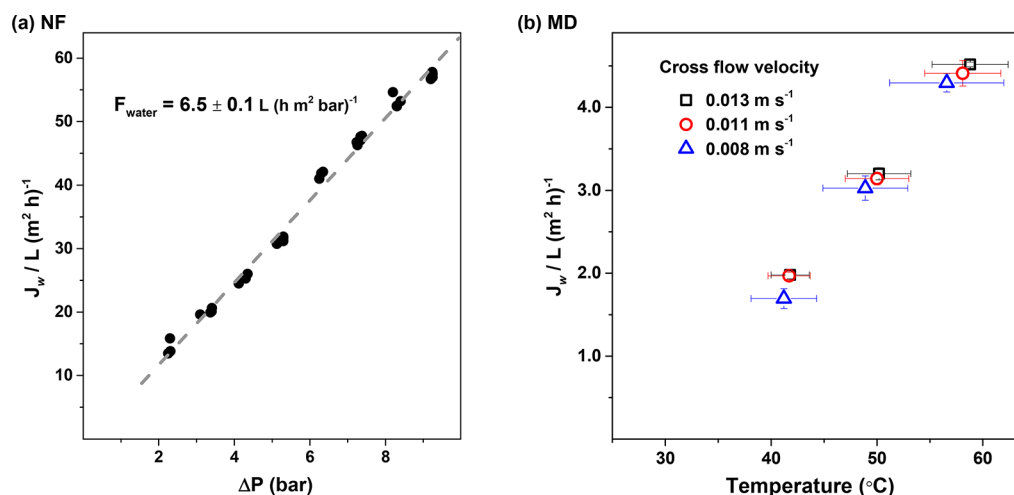
(BEVI, IEC 34–1, Sweden). Permeate mass flow was measured by a balance. Feed pressure was measured before and after the membrane by two pressure transmitters (Danfoss, MBS 4010, Denmark), and an electronic heat sensor (Kamstrup A/S, Denmark) measured feed temperature before the membrane module. A rotary lobe pump (Philipp Hilge GmbH & Co, Novalobe, Germany) controlled the cross-flow rate measured by a microprocessor-based flow rate transmitter (Siemens, MAG 50000). It was adjusted to be  $0.17\text{ L s}^{-1}$  for all the experiments. The flow rate of the retentate stream was controlled by a manual valve (Nupro). An Agilent ATR FT-IR 630 spectrophotometer with a spectral range of  $5100\text{--}640\text{ cm}^{-1}$  was employed to analyze the NF membrane after being in contact with humic substances. The spectral resolution of the equipment is lower than  $2\text{ cm}^{-1}$ , and its precision is  $0.05\text{ cm}^{-1}$ .

**2.2. Membrane Distillation Tests.** Membrane distillation tests were performed on a setup, which is illustrated elsewhere.<sup>50</sup> The feed was pumped (Cole-Parmer Masterflex L/S) to a heater (Haake K20) and afterward into the lumen side of the membrane module, and then it returned to a feed tank. The permeate was pumped (Cole-Parmer Masterflex L/S) to a cooler (Julabo FP50) and into the module in the shell side in countercurrent flow with respect to the feed. The increase of permeate volume was scrutinized by a balance (A&D Company Limited FZ-300i). The temperature was monitored in feed and permeate at the inlet and outlet of the module (Ludwig Schneider, Type 13100). The membrane module used for all experiments was made using Membrana Accurel PP S6/2 hollow fiber membranes. The outer diameter of the hollow fiber was 2.5 mm. The inner diameter was 1.6 mm, and thickness was 0.45 mm. The porosity of the membranes was 73% with a pore size of  $0.2\text{ }\mu\text{m}$ . The total membrane surface area of the 5 fibers was  $0.010\text{ m}^2$ .

**2.3. Feed Solutions and Water Analysis.** Pure water permeability was measured by filtering the deionized water that Milli-Q produced (resistivity  $> 18\text{ M}\Omega\text{ cm}$ ). For NF and MD tests, a model fluoride water solution was prepared and analyzed as follows. A Thermo Scientific Dionex ED40 instrument equipped with a conductimeter detector was used to measure the anion concentration. Anions were analyzed with an AS9HC column and a  $\text{K}_2\text{CO}_3$  solution (9 mM) as the eluent at a flow rate of  $1\text{ mL min}^{-1}$ . A PerkinElmer Optima 7000 DV ICP-Optical Emission Spectrometer (Shelton, CT, USA) equipped with WinLab 32 for ICP, version 4.0 software was used for measurement of cations. Conductivity was measured with SevenMultiTM S70-K benchtop ( $\pm 0.5\%$  accuracy). Fluoride concentration was measured with a

Table 1. Composition and Physical Properties of the Model Water System Used for Filtration Tests

		anions		cations	
conductivity (mS cm <sup>-1</sup> )	0.54	F <sup>-</sup> (mg L <sup>-1</sup> )	15.0	K <sup>+</sup> (mg L <sup>-1</sup> )	1.55
pH	6.9	Cl <sup>-</sup> (mg L <sup>-1</sup> )	24.1	Na <sup>+</sup> (mg L <sup>-1</sup> )	21.6
hardness (meq L <sup>-1</sup> )	4.45	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	16.6	Mg <sup>2+</sup> (mg L <sup>-1</sup> )	5.88
humic acid (mg L <sup>-1</sup> )	5.0	NO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	24.1	Ca <sup>2+</sup> (mg L <sup>-1</sup> )	79.24



**Figure 2.** Filtration of deionized water. (a) Permeate flux ( $J_w$ ) as a function of membrane overpressure in NF; the linear fitting of the experimental data (dashed line) was used to calculate the membrane water permeance ( $F_{\text{water}}$ ). (b)  $J_w$  of MD as a function of feed temperature: the horizontal bars and bullets indicate the temperature at the two membrane extremes and the average temperature, respectively; vertical bars indicate the standard deviation over four measurements. The permeate had an average temperature of 20 °C and the same cross-flow velocity of the feed.

fluoride selective electrode model FOO1503 (Van London, Phoenix). The X-ray diffraction (XRD) patterns of the filtered MD concentrate were acquired over a PANalytical Empyrean diffractometer, operating at 45 kV and 40 mA, with Cu K $\alpha$  radiation. The composition in Table 1 was used to simulate precipitation of salts during the concentration of the polluted feedwater. The precipitation was simulated through the geochemical software PHREEQC interactive-version 3.<sup>39</sup> A so-called “REACTION” feature in the software was utilized to remove a specified amount of water in a given number of steps. The output of the software provides information on which salts precipitate and in what amounts etc. Temperature, pH, and redox potential of the polluted water in the simulations has been assumed at 25 °C, 6.9, and 4 pe, respectively.

### 3. RESULTS AND DISCUSSION

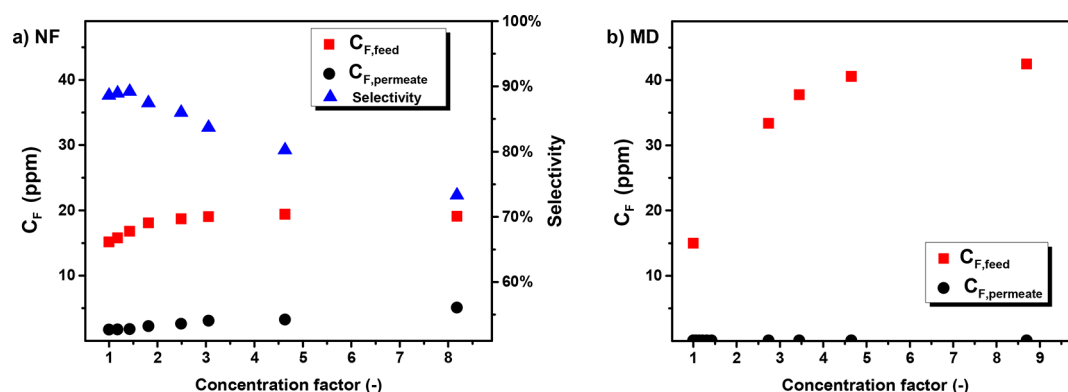
**3.1. Water Productivity.** Figure 2 allows comparing the permeate flux ( $J_w$ , L m<sup>-2</sup> h<sup>-1</sup>) of the NF and MD membranes, when deionized water (resistivity  $\geq 18 \text{ M}\Omega \text{ cm}$ ) is filtered at realistic gradients of pressure and temperature, respectively. A water permeability of  $6.5 \pm 0.1 \text{ L (m}^2 \text{ h bar)}^{-1}$  for the NF membrane was measured by fitting the experimental data in Figure 2a. This value is consistent with the water permeability reported in the literature for the other commercial NF membranes,<sup>40–48</sup> thus making this module a good basis of comparison for the MD membrane. The water fluxes achieved by the MD membrane (Figure 2b) range between 2 and 4.5 L (m<sup>2</sup> h)<sup>-1</sup> and are also in line with the literature values.<sup>49</sup> In general, the permeate flux can be increased by increasing the temperature gradient, i.e., the vapor pressure gradient across the membrane. Increasing the crossflow velocity also results in an increased flux, due to the smaller temperature drop along the membrane fiber (horizontal lines in Figure 2b). At an

average feed temperature of 58 °C and permeate temperature of 20 °C, the MD membrane can produce a flux of 4.5 L (m<sup>2</sup> h)<sup>-1</sup>, while the NF membrane has a water flux of about 60 L (m<sup>2</sup> h)<sup>-1</sup> at a transmembrane pressure ( $\Delta P$ ) of 9 bar. Therefore, the MD membrane permits the obtainment of water fluxes, which are 1 order of magnitude lower than those achieved by NF; i.e., the MD membrane requires more than 10 times larger an area to filter the same amount of water than its NF counterpart does.

Nevertheless, real water systems are complex mixtures of inorganic ions and organic molecules and often contain biological materials.<sup>50</sup> Therefore, the two membranes should be compared for their permeability and their selectivity toward fluoride ions, in such types of systems. Moreover, they should be able to maintain their perm-selectivity during filtration. For this reason, a model water system simulating fluoride-contaminated water was prepared and filtered over both the commercial NF membrane and the MD membrane. The chemical and physical properties of this water system are reported in Table 1. Such a water system had a total conductivity of 0.54 mS cm<sup>-1</sup>, a pH of 6.9, and a total hardness of 4.45 mequiv L<sup>-1</sup>. The concentrations of fluoride and humic substances were 15.0 and 5 mg L<sup>-1</sup>, respectively. The filtration performances of the two membranes during the concentration of the feed solution were investigated by measuring their permeate flux ( $J_w$ ) and by comparing retentate and permeate for their concentration of fluoride ions, dissolved ions, and humic substances.

**3.2. Fluoride Selectivity.** The fluoride concentration in the feed and in the permeate of the NF membrane was measured by a specific electrode and plotted as a function of the concentration factor (initial feed volume/volume of the feed solution during filtration) in Figure 3a. When filtration



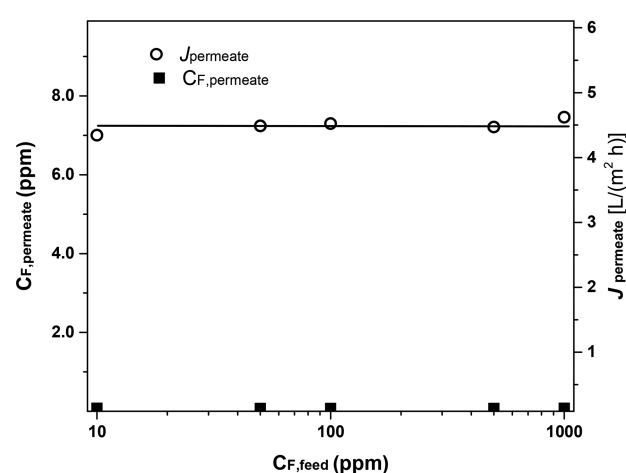


**Figure 3.** Fluoride concentration in the feed and in the permeate during concentration of the model water system in Table 1. (a) Nanofiltration (NF) was performed at  $\Delta P = 9$  bar, cross-flow rate of  $0.17 \text{ L s}^{-1}$ . (b) Membrane distillation (MD) was performed at a cross-flow velocity of  $0.013 \text{ m s}^{-1}$ , and the average temperatures of the feed side and side were  $58$  and  $20$  °C, respectively. The initial volumes of feed and permeate were  $2.4$  and  $0.40 \text{ L}$ , respectively.

started, a fluoride concentration in the permeate ( $C_{F,\text{permeate}}$ ) of  $1.7 \text{ ppm}$  was measured, corresponding to a selectivity ( $1 - C_{F,\text{permeate}}/C_{F,\text{feed}}$ ) of about  $89\%$ . The quality of the NF permeate strongly changes during the concentration of the model water system. For instance,  $C_{F,\text{permeate}}$  is about  $2.4 \text{ ppm}$  for a feed concentration factor of  $2$  and  $>3 \text{ ppm}$  for a feed concentration factor of  $3$ . Such a permeate is not suitable for human consumption. This result is not surprising, since NF membranes are known to be partially permeable to  $\text{F}^-$  ions.<sup>51–53</sup> Therefore, they are neither suitable to filter feeds with a high concentration of fluoride ions nor to achieving high concentration factors. Moreover, the membrane selectivity decreases during filtration, as shown by the blue triangles in Figure 3a. The decrease in the  $\text{F}^-$  retention with increasing the feed concentration factor can be explained by the well-known concentration polarization phenomena, which becomes more relevant at high ion concentration.

Despite the low water productivity, MD shows a higher ability to decrease the concentration of fluoride ions than NF. Indeed, the concentration of the  $\text{F}^-$  ions remained below the detection limit of our electrode ( $0.2 \text{ ppm}$ ) even after reaching a concentration factor of  $9$  (Figure 3b). In order to appreciate the selectivity of the MD membrane, model solutions with a  $\text{F}^-$  concentration ranging from  $10$  to  $1000 \text{ ppm}$  were prepared by dissolving NaF in deionized water and were tested with the same  $\Delta T$  and initial feed and permeate volumes as the previous experiment. The fluoride concentration in the permeate tank and the permeate flux are reported in Figure 4 as a function of the fluoride concentration in the feed. These data show that the membrane can completely retain  $\text{F}^-$  ions also for feeds with concentrations as high as  $1 \text{ g L}^{-1}$ . Moreover, in the absence of hardness ions, the permeate flux is not affected by the  $\text{F}^-$  concentration in the feed solutions.

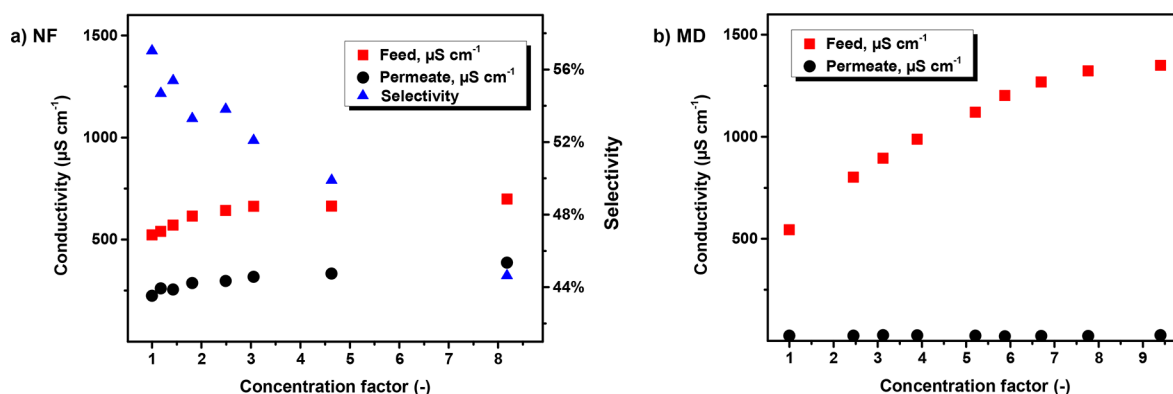
**3.3. Scaling and Salt Retention.** By observing the data points in Figure 3, we can notice that surprisingly the concentration of the  $\text{F}^-$  ions in the feed tank does not increase linearly with the feed concentration factor, but it reaches a plateau, which corresponds to about  $20 \text{ ppm}$  (from a concentration factor =  $3$ ) for NF and to about  $40 \text{ ppm}$  (from a concentration factor =  $5$ ) for MD. This can be explained by considering the hardness of our water system ( $4.45 \text{ mequiv L}^{-1}$ ) and the scarce solubility of  $\text{CaF}_2$ , which is  $24.2 \text{ ppm}$  at  $25$  °C.<sup>54</sup> Therefore, we can expect that  $\text{CaF}_2$  crystals will form during filtration and will eventually



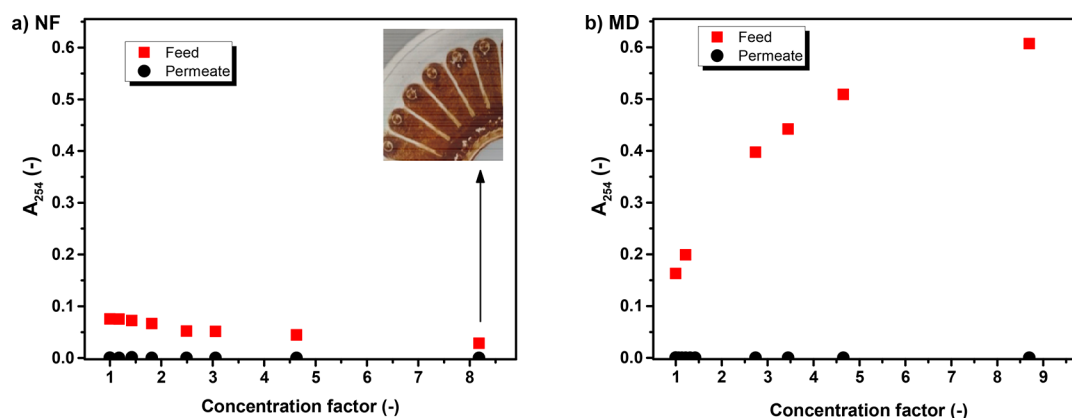
**Figure 4.** Filtration of deionized water contaminated with fluorine: measured fluoride concentration in the permeate ( $C_{F,\text{permeate}}$ ) and permeate flux ( $J_w$ ) as a function of the fluoride concentration in the feed tank ( $C_{F,\text{feed}}$ ) for the MD membrane. The experiment was performed at a cross-flow velocity of  $0.013 \text{ m s}^{-1}$ , and the average temperatures of the feed side and permeate side were  $58$  and  $20$  °C, respectively. The initial volumes of feed and permeate were  $2.4$  and  $0.40 \text{ L}$ , respectively.

precipitate on the membrane surface, in the feed tank or in the tubing.

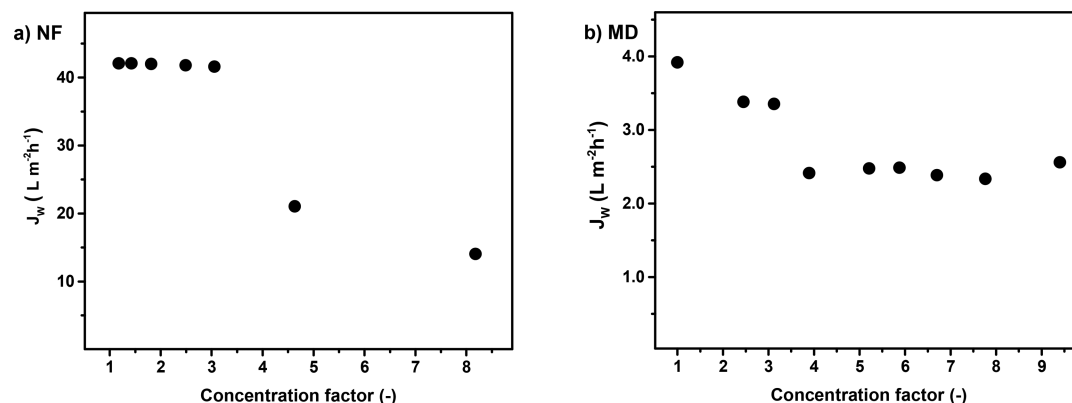
Hardness ions, such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , are notorious scaling agents, because they forms scarcely soluble salts with  $\text{F}^-$  and several other anions such as  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . Precipitation of  $\text{CaCO}_3$  and other scaling salts can be indirectly observed by measuring the conductivity of the feed and of the permeate, since it gives an estimation of the total free ions in solution. During NF, a constant conductivity is reached for concentration factors higher than  $3$  (Figure 5a), as for the fluoride ions (Figure 3a). Scaling is negative for the NF filtration performances, since it can reduce the permeate flux and screen the negative charge of the membrane surface,<sup>55</sup> thus reducing the retention of the negative  $\text{F}^-$  ions. On the contrary, the high temperature of the MD feed solution ( $\sim 58$  °C) hinders the precipitation of inorganic salts, and the concentration of the free ions at a concentration factor of  $8$  (Figure 5b) is nearly  $3$  times higher than that measured for the NF membrane (Figure 5a).



**Figure 5.** Conductivity of the feed and of the permeate during concentration of the model water system in Table 1. (a) Nanofiltration (NF) was performed at  $\Delta P = 9$  bar and crossflow rate of  $0.17 \text{ L s}^{-1}$ . (b) Membrane distillation (MD) was performed at a cross-flow velocity of  $0.013 \text{ m s}^{-1}$ , and the average temperatures of the feed side and permeate side were 58 and  $20^\circ\text{C}$ , respectively. The initial volumes of feed and permeate were 2.4 and 0.40 L, respectively.



**Figure 6.** Light absorbance at 254 nm ( $A_{254}$ ) of the feed and of the permeate during concentration of the model water system in Table 1. (a) Nanofiltration (NF) was performed at  $\Delta P = 9$  bar, cross-flow rate of  $0.17 \text{ L s}^{-1}$ ; the picture in the inset shows a portion of the surface of the polymeric NF membrane at the end of the experiment. (b) Membrane distillation (MD) was performed at a cross-flow velocity of  $0.013 \text{ m s}^{-1}$ , and the average temperatures of the feed side and permeate side were 58 and  $20^\circ\text{C}$ , respectively. The initial volumes of feed and permeate were 2.4 and 0.40 L, respectively.



**Figure 7.** Permeate flux ( $J_w$ ) during concentration of the model water system in Table 1. (a) Nanofiltration (NF) was performed at  $\Delta P = 9$  bar, cross-flow rate of  $0.17 \text{ L s}^{-1}$ ; the picture in the inset shows a portion of the surface of the polymeric NF membrane at the end of the experiment. (b) Membrane distillation (MD) was performed at a cross-flow velocity of  $0.013 \text{ m s}^{-1}$ , and the temperatures of the feed side and permeate side were 58 and  $20^\circ\text{C}$ , respectively. The initial volumes of feed and permeate were 2.4 and 0.40 L, respectively.

Figure 5a also shows that the NF membrane can only partially retain the dissolved ions. This is not surprising since NF membranes are known to have higher rejection toward polyvalent than toward monovalent ions. The total salt retention, here estimated from the ratio between the

conductivity of the permeate and of the retentate, is about 57% when filtration started. Then, a steady decline in salt retention is observed, which is probably due to the polarization phenomena and to the precipitation of salt crystals on the membrane surface, as discussed above for the retention toward

fluoride ions. On the contrary, the permeation of inorganic ions is negligible for the MD membrane, also when high concentration factors are reached (Figure 5b). Here, it should be stressed that, while the retention of the potentially harmful fluoride ions is desired, the composition of the MD permeate is not suitable for human consumption, due to its low salinity. Therefore, when MD is used for the production of drinking water, additional costs should be considered to adjust the permeate salinity.

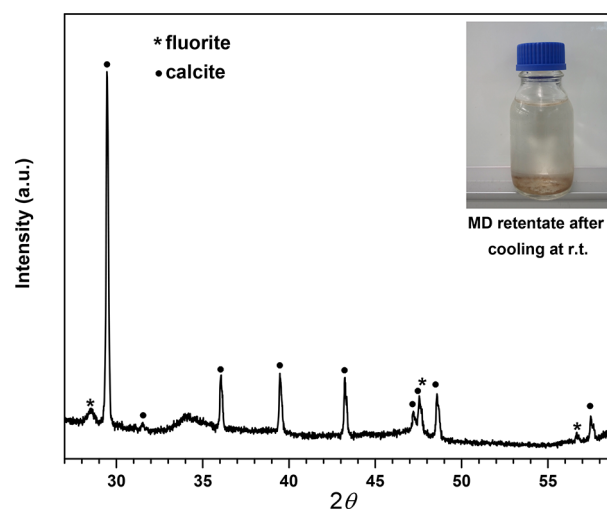
**3.4. Fouling and Permeate Flux.** As scaling is often combined with organic fouling, our model system was spiked with humic substances (HA) at a concentration of 5 mg L<sup>-1</sup>. HA molecules are common foulants, which can bind to membrane surface, blocking the membrane pores. The concentration of humic acid in the feed and in the permeate was investigated by spectrophotometric analysis.  $A_{254}$  is the absorbance of the solution at 254 nm, which is a good indicator for the concentration of humic substance in our model system. The data reported in Figure 6 point out that both membranes can completely retain HA molecules as their permeates have  $A_{254} \sim 0.0$ , regardless of the concentration factor. However, the light absorption  $A_{254}$  of the NF concentrate in the feed tank shows an unexpected trend: it decreases during filtration. The filtration was stopped after reaching a concentration factor of  $\sim 8$ . At this point, the membrane surface was inspected, revealing a brown deposit, which can be observed in the inset of Figure 6a.

Again, the MD membrane has a different behavior compared to NF. The HA concentration in the MD feed tank increases during concentration (Figure 6b). However, this trend is not linear, and therefore it cannot be excluded that part of the HA molecules start being adsorbed on the membrane surface at high concentration factors. Indeed, the amphiphilic character of the humic substances allows them to interact with both the highly hydrophilic NF and the hydrophobic MD membranes.

Figure 7 depicts the permeate flux as a function of the concentration factor for (a) the NF membrane and (b) the MD membrane. Both membranes show a flux decline during filtration. However, since the two membranes have a different interaction with the humic acid and function under different driving forces, they show different fouling behavior. As observed in Figure 6a, the permeate flux of the NF membrane at the beginning of the filtration is 42 L (m<sup>2</sup> h)<sup>-1</sup> at  $\Delta P = 9$  bar; that is only 72% of that measured for the demineralized water. This can be ascribed to an increase of the osmotic pressure across the membrane, due to the high ionic strength of the feed solution, and to the membrane fouling, which in our system is caused by the accumulation of humic substances on the surface of the membrane. Moreover, when a concentration factor of 3 is reached, the permeate flux of the NF membrane has an abrupt drop, and at a concentration factor of  $\sim 8$ ,  $J_W$  is equal to only 14 L (m<sup>2</sup> h)<sup>-1</sup>. This change is probably due to the scaling of the membrane surface, as we indirectly observed salt precipitation from the measurement of the fluoride concentration and the conductivity of the NF concentrate in Figure 3a and Figure 5a, respectively. The permeate flux decrement for the MD membrane is less pronounced compared to the NF membrane. When compared to the filtration of demineralized water,  $J_W$  is equal to 90% at the beginning of the filtration and to 55% when a concentration factor of about 9 is reached.

**3.5. Salts in the MD Concentrate.** While most of the HA molecules and the precipitated salts deposit on the NF

membrane surface during filtration, those remain dispersed in the feed solution when the model water system is treated by MD. Thus, after the filtration experiment, the MD concentrate was let to cool at room temperature. A picture of it is reported in the inset of Figure 8. At the bottom of the flask, we can see a



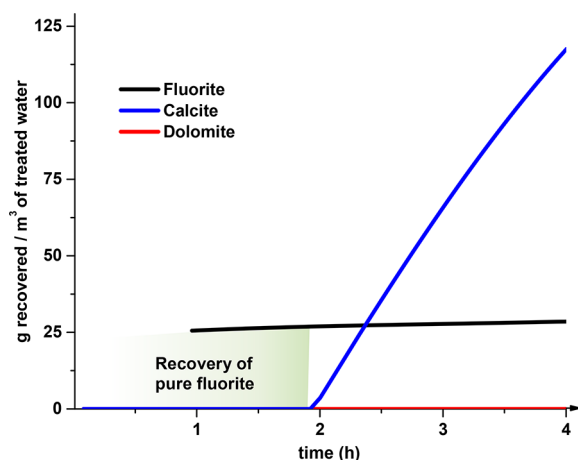
**Figure 8.** XRD pattern of the crystals in the MD concentrate, which showed in the inset picture.

brown precipitate, which must consist of insoluble humate salts (e.g., calcium and magnesium humate<sup>56,57</sup>) and mineral crystals. The precipitate was filtered over a paper filter and analyzed at the X-ray diffractometer. The diffraction pattern (Figure 8) was used to investigate the composition of the salt crystals precipitated after cooling the MD concentrate. Such analysis was performed with the “search and match” function of the software HighScore Plus (PANalytical 2017). The peaks of our diffractogram were compatible with only two types of crystals: fluorite (CaF<sub>2</sub> ref 58, peaks at  $2\theta = 28.57^\circ$ ,  $47.52^\circ$ , and  $56.4^\circ$ ) and calcite (CaCO<sub>3</sub> refs 59, 60 or Ca<sub>0.94</sub>Mg<sub>0.06</sub>CO<sub>3</sub> ref 60, peaks at  $2\theta = 29.5^\circ$ ,  $31.6^\circ$ ,  $36.1^\circ$ ,  $39.6^\circ$ ,  $43.3^\circ$ ,  $47.2^\circ$ ,  $47.6^\circ$ ,  $48.6^\circ$ , and  $57.5^\circ$ ). The reference diffractograms of other minerals cannot be matched with the peaks in Figure 8. This is consistent with the solubility product constants (at 25 °C)<sup>61</sup> of the salts that can be formed by concentration of the model water system in Table 1: CaF<sub>2</sub>  $1.7 \times 10^{-14}$ , CaCO<sub>3</sub>  $4.7 \times 10^{-9}$ , MgF<sub>2</sub>  $8 \times 10^{-8}$ , MgCO<sub>3</sub>  $4.0 \times 10^{-5}$ , CaSO<sub>4</sub>  $2.5 \times 10^{-5}$ .

The low solubility of fluorite (CaF<sub>2</sub>) makes it possible to aim for its selective recovery from MD concentrate, as shown by the simulation in Figure 9. If we consider a mixture with the composition reported in Table 1, fluorite is the first mineral salt that precipitates during concentration. The filtration can be stopped before the formation of a significant amount of calcite, thus allowing for the recovery of pure fluorite crystals from the MD concentrate.

## 4. CONCLUSIONS

In summary, both NF and MD allow for the rejection of fluoride ions in solution. However, these two processes are based on different mechanisms of permeation and selectivity, and thus they show different performances during concentration of fluoride-contaminated water. The NF membrane is partially permeable to the fluoride ions, and therefore it is not suitable to treat streams with high fluoride concentration, and at high concentration factors, the permeate might have a



**Figure 9.** MD can be used to recover pure fluorite upon partial concentration of fluoride-contaminated water. The x-axes indicate the filtration time for 1 m<sup>3</sup> of a fluoride-contaminated water (Table 1) over a MD membrane of the same type which was used in our experiment and an area of 50 m<sup>2</sup>. The y-axes indicate the amount of salt that can be recovered from the concentrate.

fluoride concentration not suitable for human consumption. However, it has much higher water productivity than the MD unit, even after the membrane surface underwent scaling and fouling.

The most important feature of MD is that the feed quality remains constant over all of the filtration time, and the fluoride concentration in our permeate was below the detection limit of our electrode (0.2 ppm), even after reaching a concentration factor of 9. MD has higher resistance to fouling and scaling than NF. Moreover, it does not require high pressure, and solar heat or waste heat can be exploited to generate a vapor pressure gradient across the membrane. The main drawbacks of MD have been proven to be (i) the low water productivity and (ii) the scarce salinity of the permeate, which must be increased at a level safe for human consumption. However, such problems are already faced by the current RO installations.

The results here reported suggest that the synergic combination of the two techniques can be an interesting solution to treat fluoride-contaminated water. At first, NF can be used to purify water until the concentration of fluoride ions in the permeate is compatible with the local requirements for drinking water, or until fouling and scaling make it inconvenient to continue the concentration process, even with frequent backwashing. Indeed, NF membranes are partially permeable to fluoride ions, and the quality of the produced drinking water deteriorates during concentration. Therefore, the NF concentrate can be further treated by MD. Preconcentration by NF will be beneficial for the MD process by reducing the energy consumption for the heating and the membrane area. Highly pure CaF<sub>2</sub> can be crystallized by cooling the MD concentrate, and eventually can be exploited in industrial processes, such as the production of hydrogen fluoride. Moreover, the permeates of the NF and MD module can be mixed to obtain a high quality drinking water, with the desired concentration of fluoride ions and dissolved minerals.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: vb@bio.aau.dk.

## ORCID

Vittorio Boffa: 0000-0001-9594-284X

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the European Commission for supporting the secondments of L. I. Moran Ayala and V. Boffa (MAT4TREAT, H2020-MSCA-RISE-2014, grant n. 64555), and for funding the PhD stipend of K. Janowska (AQUALITY, H2020-MSCA-ITN-2016, grant n. 765860). L. I. Moran Ayala thanks CONICET (Argentina) for her graduate studentship. G. N. Bosio and D. O. Mártire are research members and thank CONICET (Argentina) and CIC (Buenos Aires, Argentina), respectively.

## REFERENCES

- (1) Choubisa, S. L. Fluorosis in some tribal villages of Dungapur district of Rajasthan. *India. Fluoride* **1997**, *30*, 223–228.
- (2) Xu, R. Q.; Wu, D. Q.; Xu, R. Y. Relations between environment and endemic fluorosis in Hohot region, Inner Mongolia. *Fluoride* **1997**, *30*, 26–28.
- (3) Ali, S.; Thakur, S. K.; Sarkar, A.; Shekhar, S. Worldwide contamination of water by fluoride. *Environ. Chem. Lett.* **2016**, *14*, 291–315.
- (4) *Guidelines for Drinking-Water Quality*, first addendum to third ed., vol. 1, recommendations; WHO: 2006.
- (5) Murray, J. J. *Appropriate use of fluorides for human health*; World Health Organization: Geneva, 1986.
- (6) Ayoob, S.; Gupta, A. K.; Bhat, V. T. A conceptual overview on sustainable technologies for the defluoridation of drinking water. *Crit. Rev. Environ. Sci. Technol.* **2008**, *38*, 401–470.
- (7) Ben Nasr, A.; Charcosset, C.; Ben Amar, R.; Walha, K. Defluoridation of water by nanofiltration. *J. Fluorine Chem.* **2013**, *150*, 92–97.
- (8) Boussouga, Y. A.; Lhassani, A. Modeling of fluoride retention in nanofiltration and reverse osmosis membranes for single and binary salt mixtures. *Desalination Water Treat.* **2017**, *95*, 162–169.
- (9) Owusu-Agyeman, I.; Jeihanipour, A.; Luxbacher, A. T.; Schafer, A. I. Implications of humic acid, inorganic carbon and speciation on fluoride retention mechanisms in nanofiltration and reverse osmosis. *J. Membr. Sci.* **2017**, *528*, 82–94.
- (10) Al-Harashsheh, M.; Hussain, Y. A.; Al-Zoubi, H.; Batiha, M.; Hammouri, E. Hybrid precipitation-nanofiltration treatment of effluent pond water from phosphoric acid industry. *Desalination* **2017**, *406*, 88–97.
- (11) Shen, J. J.; Richards, B. S.; Schafer, A. I. Renewable energy powered membrane technology: Case study of St. Dorcas borehole in Tanzania demonstrating fluoride removal via nanofiltration/reverse osmosis. *Sep. Purif. Technol.* **2016**, *170*, 445–452.
- (12) Shen, J. J.; Schafer, A. I. Factors affecting fluoride and natural organic matter (NOM) removal from natural waters in Tanzania by nanofiltration/reverse osmosis. *Sci. Total Environ.* **2015**, *527*, 520–529.
- (13) Shen, J. J.; Schafer, A. I. Removal of fluoride and uranium by nanofiltration and reverse osmosis: A review. *Chemosphere* **2014**, *117*, 679–691.
- (14) Xi, B. D.; Wang, X. W.; Liu, W. J.; Xia, X. F.; Li, D. S.; He, L. S.; Wang, H. M.; Sun, W. J.; Yang, T. X.; Tao, W. Fluoride and Arsenic Removal by Nanofiltration Technology from Groundwater in Rural Areas of China: Performances with Membrane Optimization. *Sep. Sci. Technol.* **2014**, *49*, 2642–2649.
- (15) Bejaoui, I.; Mnif, A.; Hamrouni, B. Performance of Reverse Osmosis and Nanofiltration in the Removal of Fluoride from Model Water and Metal Packaging Industrial Effluent. *Sep. Sci. Technol.* **2014**, *49*, 1135–1145.



- (16) Chakraborty, S.; Roy, M.; Pal, P. Removal of fluoride from contaminated groundwater by cross flow nanofiltration: Transport modeling and economic evaluation. *Desalination* **2013**, *313*, 115–124.
- (17) Hoinkis, J.; Valero-Freitag, S.; Caporgno, M. P.; Patzold, C. Removal of nitrate and fluoride by nanofiltration - a comparative study. *Desalin. Water Treat.* **2011**, *30*, 278–288.
- (18) Bejaoui, I.; Mnif, A.; Hamrouni, B. Influence of operating conditions on the retention of fluoride from water by nanofiltration. *Desalin. Water Treat.* **2011**, *29*, 39–46.
- (19) Wang, X. W.; Xi, B. D.; Huo, S. L.; Liu, W. J.; Sun, W. J.; Li, D. S.; Yu, H. B.; Ma, W. F.; Liu, H. L. Performances comparison of reverse osmosis and nanofiltration application to defluorination from groundwater: influence factors and fouling analysis. *Fresenius Environ. Bull.* **2011**, *20*, 3141–3151.
- (20) Padilla, A. P.; Saitua, H. Performance of simultaneous arsenic, fluoride and alkalinity (bicarbonate) rejection by pilot-scale nanofiltration. *Desalination* **2010**, *257*, 16–21.
- (21) Nightingale, E. R. Phenomenological theory of ion solvation. Effective radii of hydrated ions. *J. Phys. Chem.* **1959**, *63*, 1381–1387.
- (22) Zhou, J.; Lu, X.; Wang, Y.; Shi, J. Molecular dynamics study on ionic hydration. *Fluid Phase Equilib.* **2002**, *194–197*, 257–270.
- (23) Kiriukhin, M. Y.; Collins, K. D. Dynamic hydration numbers for biologically important ions. *Biophys. Chem.* **2002**, *99*, 155–168.
- (24) Farsi, A.; Malvache, C.; De Bartolis, O.; Magnacca, G.; Kristensen, P. K.; Christensen, M. L.; Boffa, V. Design and fabrication of silica-based nanofiltration membranes for water desalination and detoxification. *Microporous Mesoporous Mater.* **2017**, *237*, 117–126.
- (25) Farsi, A.; Boffa, V.; Christensen, M. L. Electroviscous effects in ceramic nanofiltration membranes. *ChemPhysChem* **2015**, *16*, 3397–407.
- (26) Farsi, A.; Boffa, V.; Qureshi, H. F.; Nijmeijer, A.; Winnubst, L.; Christensen, M. L. Modeling water flux and salt rejection of mesoporous  $\gamma$ -alumina and microporous organosilica membranes. *J. Membr. Sci.* **2014**, *470*, 307–315.
- (27) Diawara, C. K. Nanofiltration Process Efficiency in Water Desalination. *Sep. Purif. Rev.* **2008**, *37*, 302–324.
- (28) Qtaishat, M. R.; Banat, F. Desalination by solar powered membrane distillation systems. *Desalination* **2013**, *308*, 186–197.
- (29) Quist-Jensen, C. A.; Ali, A.; Mondal, S.; Macedonio, F.; Drioli, E. A study of membrane distillation and crystallization for lithium recovery from high-concentrated aqueous solutions. *J. Membr. Sci.* **2016**, *505*, 167–173.
- (30) Hou, D. Y.; Wang, J.; Wang, B. Q.; Luan, Z. K.; Sun, X. C.; Ren, X. J. Fluoride removal from brackish groundwater by direct contact membrane distillation. *Water Sci. Technol.* **2010**, *61*, 3178–3187.
- (31) Hou, D.; Wang, J.; Zhao, C.; Wang, B.; Luan, Z.; Sun, X. Fluoride removal from brackish groundwater by direct contact membrane distillation. *J. Environ. Sci.* **2010**, *22*, 1860–1867.
- (32) Boubakri, A.; Bouchrit, R.; Hafiane, A.; Al-Tahar Bouguecha, S. Fluoride removal from aqueous solution by direct contact membrane distillation: theoretical and experimental studies. *Environ. Sci. Pollut. Res.* **2014**, *21*, 10493–10501.
- (33) Qtaishat, M.; Rana, D.; Matsuura, T.; Khayet, M. Effect of surface modifying macromolecules stoichiometric ratio on composite hydrophobic/hydrophilic membranes characteristics and performance in direct contact. *AIChE J.* **2009**, *55*, 3145–3151.
- (34) Qtaishat, M.; Khayet, M.; Matsuura, T. Novel porous composite hydrophobic/hydrophilic polysulfone membranes for desalination by direct contact membrane distillation. *J. Membr. Sci.* **2009**, *341*, 139–148.
- (35) Qtaishat, M.; Matsuura, T.; Khayet, M.; Khulbe, K. C. Comparing the desalination performance of SMM blended polyethersulfone to SMM blended polyetherimide membranes by direct contact membrane distillation. *Desalin. Water Treat.* **2009**, *5*, 91–98.
- (36) Boubakri, A.; Hafiane, A.; Bouguecha, S. A. T. Application of response surface methodology for modeling and optimization of membrane distillation desalination process. *J. Ind. Eng. Chem.* **2014**, *20*, 3163–3169.
- (37) Ali, A.; Macedonio, F.; Drioli, E.; Aljlil, S.; Alharbi, O. A. Experimental and theoretical evaluation of temperature polarization phenomenon in direct contact membrane distillation. *Chem. Eng. Res. Des.* **2013**, *91*, 1966–1977.
- (38) Meschke, K.; Daus, B.; Haseneder, R.; Repke, J.-U. Strategic elements from leaching solutions by nanofiltration – Influence of pH on separation performance. *Sep. Purif. Technol.* **2017**, *184*, 264–274.
- (39) Parkhurst, D. L.; Appelo, C. A. Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. Available online: <http://pubs.usgs.gov/tm/06/a43>.
- (40) FILMTEC XLE-2521 Membranes, Form No. 609-00349-0706. [www.lenntech.com/Data-sheets/Dow-Filmtec-XLE-2521.pdf](http://www.lenntech.com/Data-sheets/Dow-Filmtec-XLE-2521.pdf).
- (41) FLUID SYSTEMS® TFC®-ULP® 4" ELEMENT, KOCH membrane system. [www.lenntech.com/Data-sheets/Koch-Fluid-Systems-TFC-4040-ULP-L.pdf](http://www.lenntech.com/Data-sheets/Koch-Fluid-Systems-TFC-4040-ULP-L.pdf).
- (42) Toray Membrane Product. [www.toraywater.com/products/ro/pdf/TMG.pdf](http://www.toraywater.com/products/ro/pdf/TMG.pdf).
- (43) Hydranautics Corporate. <http://www.membranes.com/docs/4inch/ESPA4-4040.pdf>.
- (44) FILMTEC Membranes, Nanofiltration Produces Sparkling Clean Water for Swedish Resort Community, Form No. 609-00379-0503. [http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh\\_0047/0901b803800478f5.pdf?filepath=liquidseps/pdfs/noreg/609-00379.pdf&fromPage=GetDoc](http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0047/0901b803800478f5.pdf?filepath=liquidseps/pdfs/noreg/609-00379.pdf&fromPage=GetDoc).
- (45) FILMTEC Membranes, FILMTEC NF90-400 Nanofiltration Element, Nanofiltration Elements for Commercial Systems, Form No. 609-00345-0406. <http://www.lenntech.com/Data-sheets/Dow-Filmtec-NF90-400.pdf>.
- (46) CK Series, Water Softening NF Elements (Cellulose Acetate), GE water & process technology. [https://www.gewater.com/kcpguest/salesedge/documents/Fact%20Sheets\\_Cust/Americas/English/FS1268EN.pdf](https://www.gewater.com/kcpguest/salesedge/documents/Fact%20Sheets_Cust/Americas/English/FS1268EN.pdf).
- (47) Hydranautics Corporate. <http://www.membranes.com/docs/8inch/ESNA1-LF-LD.pdf>.
- (48) Product Guide for Spiral-Wound RO & NF Elements, CSM. [http://www.csmfilter.com/csm/upload/RO\\_Catalogue/CSM%20RO%20Catalog\\_Eng\\_Final\\_DavidK\\_11.7.12.pdf](http://www.csmfilter.com/csm/upload/RO_Catalogue/CSM%20RO%20Catalog_Eng_Final_DavidK_11.7.12.pdf).
- (49) Ullah, R.; Khraisheh, M.; Esteves, R. J.; McLeskey, J. T.; AlGhouthi, M.; Gad-El-Hak, M.; Tafreshi, H. V. Energy efficiency of direct contact membrane distillation. *Desalination* **2018**, *433*, 56–67.
- (50) Quist-Jensen, C. A.; Sørensen, J. M.; Svenstrup, A.; Scarpa, L.; Carlsen, T. S.; Jensen, H. C.; Wybrandt, L.; Christensen, M. L. Membrane crystallization for phosphorus recovery and ammonia stripping from reject water from sludge dewatering process. *Desalination* **2018**, *440*, 156.
- (51) Perez Padilla, A.; Saitua, H. Performance of simultaneous arsenic, fluoride and alkalinity (bicarbonate) rejection by pilot-scale nanofiltration. *Desalination* **2010**, *257*, 16–21.
- (52) Richards, L. A.; Richards, B. S.; Rossiter, H. M. A.; Schäfer, A. I. Impact of speciation on fluoride, arsenic and magnesium retention by nanofiltration/reverse osmosis in remote, Australian communities. *Desalination* **2009**, *248*, 177–183.
- (53) Shen, J.; Schäfer, A. Removal of fluoride and uranium by nanofiltration and reverse osmosis: A review. *Chemosphere* **2014**, *117*, 679–69.
- (54) McCann, H. G. The solubility of fluorapatite and its relationship to that of calcium fluoride. *Arch. Oral Biol.* **1968**, *13*, 987–1001.
- (55) Tu, K. L.; Chivas, A. R.; Nghiem, L. D. Effects of membrane fouling and scaling on boron rejection by nanofiltration and reverse osmosis membranes. *Desalination* **2011**, *279*, 269–277.
- (56) Kříženecká, S.; Hejda, S.; Machovič, V.; Trögl, J. Preparation of iron, aluminium, calcium, magnesium, and zinc humates for environmental applications. *Chemical Papers* **2014**, *68*, 1443–1451.
- (57) Savarino, P.; Montoneri, E.; Bottigliengo, S.; Boffa, V.; Guizzetti, T.; Perrone, D. G.; Mendichi, R. Biosurfactants from

urban wastes as auxiliaries for textile dyeing. *Ind. Eng. Chem. Res.* **2009**, *48*, 3738–3748.

(58) Speziale, S.; Duffy, T. S. Single-crystal elastic constants of fluorite ( $\text{CaF}_2$ ) to 9.3 GPa. *Phys. Chem. Miner.* **2002**, *29*, 465–472.

(59) Ondrus, P.; Veselovsky, F.; Gabasova, A.; Hlousek, J.; Srein, V.; Vavrn, I.; Skala, R.; Sejkora, J.; Drabek, M. Primary minerals of the Jáchymov ore district. *Journal of the Czech Geological Society* **2003**, *48*, 19–147.

(60) Paquette, J.; Reeder, R. J. Single-crystal X-ray structure refinements of two biogenic magnesian calcite crystals. *Am. Mineral.* **1990**, *75*, 1151–1158.

(61) Gupta, A. K. S. *Ion Exchange in Environmental Processes: Fundamentals, Applications and Sustainable Technology*, first ed.; John Wiley & Sons, Inc., 2017.